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*Vasyl Stefanyk Precarpathian
National University*

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V.I. Mandzyuk, I.F. Mironyuk, N.Ya. Ivanichok, B.I. Rachiy

Impedance spectroscopy of capacitor systems based on saccharide-derived porous carbon materials

Vasyl Stefanyk Precarpathian National University, 57 Shevchenko Str., Ivano-Frankivsk, 76018, Ukraine,
volodymyr.mandzyuk@pnu.edu.ua

The electrochemical processes in capacitor systems based on porous carbon materials (PCMs) derived from glucose, lactose, and saccharose at activation temperature of 800 and 1000°C are explored using impedance spectroscopy method. An equivalent electric circuit, which allows modeling of the impedance spectra in the frequency range from 10^{-2} to 10^{5} Hz, is proposed, and a physical interpretation of each element of the electrical circuit is presented. It is set that in capacitor systems on the basis of the explored materials the accumulation of capacitance occurs due to the formation of a double electric layer at the electrode/electrolyte boundary, and Faradaic processes are minimized. The specific capacity of supercapacitors based on PCMs obtained at 800°C is 91-154 F/g due to the developed microporous structure of materials.

Keywords: porous carbon material, impedance spectroscopy, supercapacitor, specific surface area, equivalent electric circuit.

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Introduction

Supercapacitors (SCs), also called as ultracapacitors or ionistors, are a high-capacity electrochemical devices with capacitance values much higher than other capacitors. To achieve capacitances several orders of magnitude larger than conventional capacitors, SCs utilize high surface area electrode materials and very thin dielectrics [1-4].

SCs can be divided into three general classes: electrochemical double-layer capacitors (EDLCs), pseudocapacitors, and hybrid capacitors. Each class is characterized by its mechanism for charge storage: non-Faradaic, Faradaic, and a combination of the two, respectively. EDLCs use of high surface area carbon materials like as activated carbon [5-7], carbon nanotubes [8, 9], carbon aerogels [10, 11]. Pseudocapacitors use transition metal oxide [12, 13] or conducting polymer [14, 15] as electrodes. And hybrid capacitors are having asymmetric electrodes, of which one has electrostatic and the other has electrochemical capacitance [16, 17]. Utilizing both Faradaic and non-Faradaic processes to store charge, hybrid capacitors have achieved energy and power densities greater than EDLCs without the sacrifices in cycling stability and affordability that have limited the success of pseudocapacitors.

However, there are cases when the accumulation of electric charge on the surface of the electrode material occurs due to Faradaic and non-Faradaic processes. This is achieved by doping processes of the electrode material, primarily porous carbon, heteroatoms N-, B-, O-, P-, S-. As a result, hydrophilic functional groups are formed on the material surface, which improve the wettability of the electrode and, consequently, increase the capacitor perfomance [18-21].

Therefore, understanding the electrochemical processes that occur in capacitor systems formed on the basis of porous carbon materials (PCMs) is important. Thus, we showed by chronopotentiometry and cyclic voltammetry in [22], studying the structural-morphological and electrochemical properties of PCMs obtained by saccharide carbonization, that the electric capacity of SCs is provided by the formation of a double electric layer (DEL) at the electrode/electrolyte boundary and capacity due to redox reactions (Faradaic processes) or pseudo-capacity is absent. Additional information on the passing of electrochemical processes in capacitor systems can be obtained using the method of impedance spectroscopy, which allow to establish in more detail the relationship between the porous structure of the electrode carbon material and its behavior in aqueous electrolyte solution, which is the purpose of this work.

I. Materials and methods

Crystalline monohydrates of glucose (G), lactose (L), and anhydrous saccharose (S) were used as precursors of chars prepared at 400°C for 30 min in air. Oxidizing activation of chars was carried out in ceramic crucibles at 800 or 1000°C for 30 min. Accordingly to that the test samples were denoted as G800, L800, S800 and G1000, L1000, S1000.

The lamellar form electrodes of symetric SC were prepared from a mixture PCM:CA = 75:25, where CA is a conductive additive (KS-15 graphite (Lonza Group, Basel, Switzerland)). These symmetrical electrodes were infiltrated by the electrolyte and were separated by a separator and sealed in two-electrode cell of the size “2525”. As the electrolyte 30% KOH solution was used.

Impedance analysis of SCs was carried out using a Metrohm Autolab FRA-2 (Frequency Response Analyzer) at 10^{-2}–10^{5} Hz, voltage amplitude of 10 mV and bias potential from 0 V to 1 V with the step of 0.2 V.

The textural characteristics of PCMs (degassed at 180 °C for 24 h) have been determined using the nitrogen adsorption-desorption isotherms recorded at 77.4 K using a Quantachrome Autosorb Nova 2200e adsorption analyzer. The specific surface area (S_{BET}, m^2/g) was determined by multipoint BET-method in limited range of relative pressure $P/P_0 = 0.050 \dots 0.035$. The total pore volume (V, cm^3/g) was calculated by the number of adsorbed nitrogen at P/P_0 ~1.0. The volume of micropores (V_{micro}, cm^3/g), the values of specific surface of micro (S_{micro}, m^2/g), and mesopores (S_{meso}, m^2/g) were found using the t-method [23].

II. Results and discussion

To study the electrochemical processes that occur both at the electrode/electrolyte boundary and in the bulk electrode material is quite effective to use the method of impedance spectroscopy, as it allows to conduct research in a wide frequencies range ($f = 10^{6}$-10^{-3} Hz) [24].

The basis of structural modeling of the proposed processes on the basis of experimental data obtained by impedance spectroscopy is a systems approach. It consists in the fact that the object under study is considered as an equivalent electrical circuit (EEC), which includes elements that characterize the electrode/electrolyte phase boundary and the bulk electrode material. EEC is a simplified model of real processes in the system explored, which create resistance to electric current. The basic criterion when choosing an EEC is the integral physical content of all its structural elements under the condition of optimal approximation of experimental hodographs of impedance –Im Z = f(Re Z).

As can be seen from the impedance spectra (Fig. 1) obtained for SCs based on materials S800 and S1000, the inductive component predominates at high frequencies. When the frequency decreases, the capacitive component dominates over the inductive one. In the midrange, the Nyquist diagram has the form of a straight line inclined at an angle of about 45°, which indicates the passing of diffusion processes in the system explored. This line changes its inclination to almost vertical at low frequencies, which indicates the capacitive accumulation of electric charge.

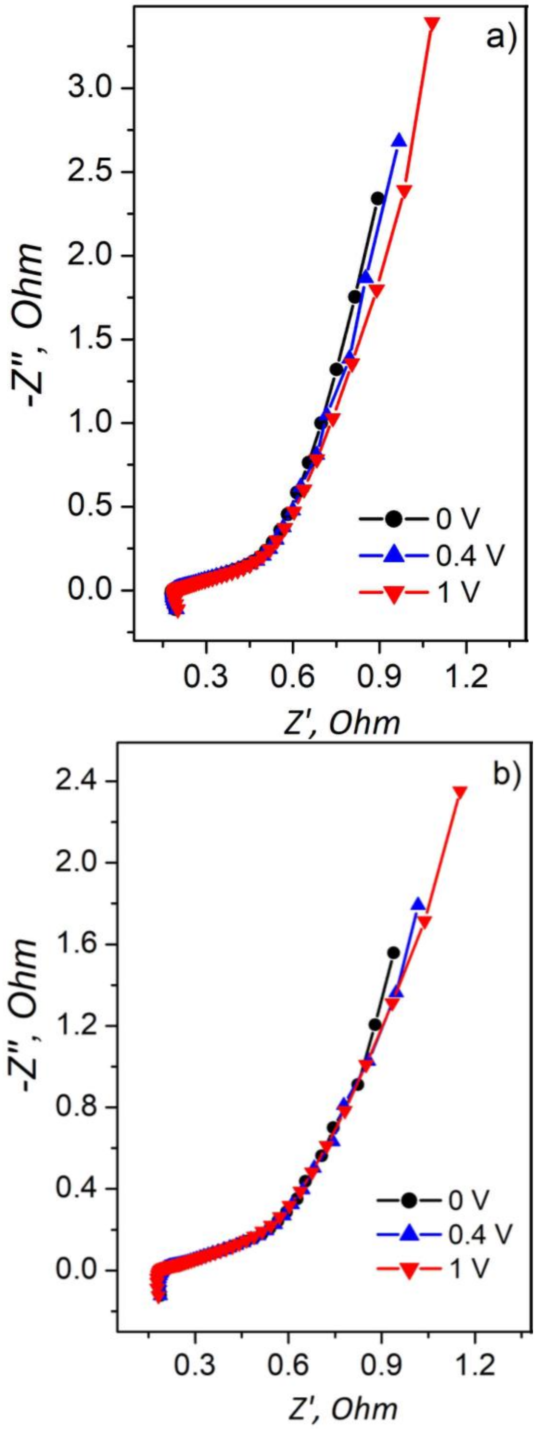

Fig. 1. The Nyquist diagrams for S800 (a) and S1000 (b) capacitor system at different bias voltages.

Based on the qualitative analysis of impedance spectra, we selected the EEC (Fig. 2), which satisfactorily describes the passing of electrochemical processes in SCs on the basis of the materials studied. The element L_1 in this circuit characterizes the inductive behavior of the electrochemical system, which is due to both the metal parts of the case and the developed porous structure of the carbon material, which is analogous to the inductance at high frequencies [25]. Element R_s includes the resistance of the electrolyte, contacts and supply wires. Other elements are responsible for the diffusion processes in the pores of PCM and the accumulation of electric charges at the electrolyte/electrode boundary. In particular, the $C_2||R_2$-link is responsible foremost for diffusion processes in the transport pores (macro- and mesopores), and $CPE_3||$ R_3-CPE_4-link for charge storage in micropores. The constant phase element (CPE) was used in the simulation of impedance hodographs. The impedance of this element is determined by the equation [24]:

$$Z_{CPE} = CPE_T \left(j\omega \right)^{-CPE_P} \qquad (1)$$

The CPE_P parameter takes into account the phase deviation and, accordingly, the type of process modeled. In particular, when CPE_P value is little less than 1, then the CPE behaviour is close to that of a capacitance; when CPE_P is close to 0.5 – diffusion one, when $CPE_P \approx -1$ – inductive one. The introduction of this element is primarily due to the fractal structure of the PCM [22] and, as a result, the inhomogeneous distribution of charge carriers at the electrode/electrolyte boundary.

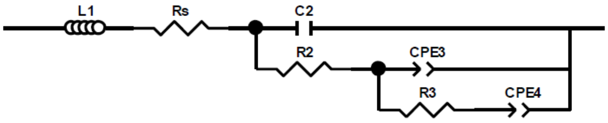

Fig. 2. The equivalent electrical circuit of capacitor systems

The most noticeable changes in the shape of the Nyquist diagram are observed in the low-frequency region when the bias voltage increases (Fig. 1). This is due to the fact that, more potassium ions participate in the DEL formation at the PCM/electrolyte boundary with increasing voltage between the electrodes, resulting in an increase in capacitor capacity.

A similar change in the shape of the impedance curves with a change in the bias voltage is characteristic of SCs formed on the basis of glucose and lactose. The difference is observed only in the values of real and imaginary components of resistance.

It should be noted that there is almost no clear depressed semicircle in the Nyquist diagrams in the high-frequency part of the spectrum, which indicates the processes of charge transfer and accumulation involving Faradaic processes or pseudocapacity. It indicates the dominance of the DEL capacity over the capacity due to the redox reactions, which confirms the results of galvanostatic and potentiodynamic cycling [22].

The use of EEC made it possible to approximate the experimental spectrum quite well to the calculated one (the difference between the experimental and model curves does not exceed 5%) and to obtain the values of the circuit parameters (Table 1).

Since the passing of electrochemical processes in SCs largely depends on the parameters of the porous structure of the electrode material (specific surface area, total pore volume and the ratio between micro- and mesopores), it is necessary to determine its changes with increasing of carbonization temperature.

As follows from the results of low-temperature porometry (Table 2), micropores dominate in PCMs obtained from lactose and saccharose at 800°C. Their specific surface area is 73 and 57%, and the volume is 70 and 49%, respectively. These values are 47 and 43% for glucose-derived PCM, respectively, indicating a slight dominance of mesopores. When the activation temperature increases to 1000°C, the most noticeable changes in the porous structure are observed for PCMs based on glucose and lactose. In particular, the specific

Table 1

EEC parameters for SCs (bias voltage 1 V)

Sample	L_1, μH	R_s, Ohm	C_2, mF	R_2, mOhm	CPE_{3T}, Ohm	CPE_{3P}	R_3, Ohm	CPE_{4T}, F	CPE_{4P}
G800	0.38	0.18	8.4	43	1.53	0.55	0.89	1.26	0.88
G1000	0.08	0.17	1.7	25	0.78	0.49	0.77	0.33	0.95
L800	0.46	0.15	6.4	16	1.15	0.56	0.64	1.65	0.92
L1000	0.62	0.16	9.6	21	1.24	0.61	0.57	1.06	0.89
S800	0.34	0.16	9.2	18	0.98	0.54	0.71	1.17	0.91
S1000	0.35	0.17	7.8	20	0.84	0.53	0.66	0.98	0.90

Table 2

Parameters of porous structure of samples according to the method of low-temperature porometry

Sample	S_{BET}, m^2/g	S_{micro}, m^2/g	S_{meso}, m^2/g	V, cm^3/g	V_{micro}, cm^3/g	V_{meso}, cm^3/g
G800	383	181	202	0.201	0.086	0.113
G1000	46	10	36	0.016	0.003	0.013
L800	437	318	119	0.232	0.162	0.070
L1000	652	497	155	0.345	0.226	0.118
S800	356	204	152	0.187	0.092	0.095
S1000	362	225	137	0.198	0.115	0.083

surface area and the total pore volume are reduced by 8 and 12 times for the G1000 sample, respectively; the part of micropores also decreases more than 2 times. The structural changes are opposite for the L1000 sample: the specific surface area increases by 50%, and the ratio between micro- and mesopores practically does not change. The specific surface area does not change for the S1000 sample, there is a slight redistribution between the micro- and mesoporous structure in the direction of a slight increase in the proportion of micropores.

Comparing the data of Tables 1 and 2, one can see a certain correlation between the values of the EEC elements and the parameters of the porous structure of the materials. SCs based on materials with a more developed porous structure are characterized by a higher value of the parameter L_1. The resistance R_s for all electrochemical systems is constant (0.15 ÷ 0.18 Ohm), because it is determined by the electrolyte concentration and the resistance of the supply wires and contacts, which are constant. Parameters C_2 and R_2, which characterize the processes of diffusion and accumulation of electric charge in mesopores, are characterized by proportional dependence. It is obvious that the more developed the system of mesopores is, the more K^+ ions will take part in the DEL formation on the mesopores surface. On the other hand, it is difficult to transport ions to the micropores, which affects the increase in resistance R_2. The CPE_3 element is a constant phase element of the diffusion type (the value of CPE_{3P} is close to 0.5), the value of which also depends on the number of micro- and mesopores and their ratio. Characteristic is the deviation of the exponent CPE_{3P} in equation (1) from the ideal value of 0.5, which is associated with the fractal structure of PCM particles [22]. The same reason causes the deviation of the parameter CPE_{4P} of capacitive type from ideal value 1, which characterizes the charge accumulation in the micropores. The value of the parameter R_3 is determined by the complex action of the diffusion resistance of K^+ ions in micropores and the ohmic resistance of PCM particles [25].

From the data in Table 1, having the value of the capacitance C_2, which accumulates in the mesopores, and the value of $Z_{CPE\text{-}4}$ of capacitive type, which characterizes the electric charge accumulation in the micropores, one can estimate the PCM capacity per unit mass, or specific material capacity (Table 3). According to impedance spectroscopy analysis, the largest specific capacity (154 F/g) has an electrode material based on porous carbon derived from lactose at an activation temperature of 800°C. This result can be attributed to a maximum micropore specific surface area of 318 m^2/g, as opposite to 181 m^2/g (for the G800 sample) and 204 m^2/g (for the S800 sample). It is characteristic that when the activation temperature increases to 1000°C, the specific capacity of materials decreases. The most noticeable changes in the value of specific capacity are observed for SCs based on samples L1000 and G1000. Given that the specific surface area due to activation increases by 50% for the sample L1000 and the entire surface is open to nitrogen molecules, one should expect an increase in the specific capacity. However, the SC based on this material shows a 43% reduction in capacity. This behavior is probably due to the fact that not the entire surface is wetted by the electrolyte and does not participate in the DEL formation due to the partial graphitization of the material. For SC based on sample G1000, the 71% decrease in specific capacity can be explained by a significant decrease in the specific surface area and total pore volume of the material (Table 2). The least noticeable changes in the value of the specific capacity (decrease by 18%) are observed for SCs based on saccharose-derived PCMs.

Table 3

Parameters of porous structure of samples according to the method of low-temperature porometry

Sample	Method		
	Chrono-potentiometry	Cyclic voltammetry	Impedance spectroscopy
G800	117	110	112
G1000	36	32	33
L800	160	154	154
L1000	91	87	88
S800	94	89	91
S1000	77	74	75

The specific capacitance values calculated by impedance spectroscopy method coincide with the results of chronopotentiometry [22] and cyclic voltammetry (the specific capacitance C of the materials was calculated using the equation

$$C = \frac{\int_{U_1}^{U_2} I(U)\,dU}{2ms\left(U_2 - U_1\right)},$$

where U_1 and U_2 are cutoff potentials in cyclic voltammetry curve [22], $I(U)$ is an instantaneous current, m is a mass of the sample, s is a scan rate) (Table 3).

Conclusions

According to impedance spectroscopy, electrochemical processes in capacitor systems based on saccharide-derived porous carbon materials are associated with the diffusion of potassium ions in transport pores (macro- and mesopores) and their accumulation at the PCM/electrolyte boundary in micropores. Capacity accumulation due to redox reactions (Faradaic processes) or pseudocapacity is absent, which confirms the results of chronopotentiometry and cyclic voltammetry.

The relation between the values of the EEC elements and the parameters of the porous structure of materials is set and their change with increasing activation temperature of PCMs is analyzed.

The values of the specific capacity of SCs are 154 F/g (L800), 112 F/g (G800) and 91 F/g (S800), which satisfactorily correlates with the size of the specific surface area and the total pore volume of these samples. When activation temperature increases to 1000°C there is a decrease in the specific capacity of SCs by 43, 71 and 18%, respectively.

Mandzyuk V.I. – Doctor in Physics and Mathematics, Associate Professor, Associate Professor of Department of Computer Engineering and Electronics;
Mironyuk I.F. – Doctor in Chemistry, Professor, Head of the Chemistry Department;
Ivanichok N.Ya. – PhD in Physics and Mathematics, Senior Specialist of Joint Educational and Scientific Laboratory for Physics of Magnetic Films of G.V. Kurdyumov Institute for Metal Physics NAS of Ukraine, State University "Precarpathian National University named after Vasyl Stefanyk", Ministry of Education and Sciences of Ukraine;
Rachiy B.I. – Doctor in Physics and Mathematics, Professor of Department of Materials Science and Emerging Technologies;

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В.І. Мандзюк, І.Ф. Миронюк, Н.Я. Іванічок, Б.І. Рачій

Імпедансна спектроскопія конденсаторних систем, на основі пористих вуглецевих матеріалів, отриманих з сахаридів

Прикарпатський національний університет імені Василя Стефаника, вул. Шевченка, 57, 76018 Івано-Франківськ,
Україна, (095)305-09-53 volodymyr.mandzyuk@pnu.edu.ua

У роботі з використанням методу імпедансної спектроскопії досліджено електрохімічні процеси в конденсаторних системах на основі пористих вуглецевих матеріалів (ПВМ), отриманих із глюкози, лактози і сахарози за температур активації 800 та 1000°С. Запропоновано еквіваленту електричну схему, яка дозволяє задовільно моделювати імпедансні спектри в діапазоні частот 10^{-2} – 10^{5} Гц та подано фізичну інтерпретацію кожного елемента електричної схеми. Встановлено, що в конденсаторних системах на основі досліджуваних матеріалів накопичення ємності відбувається за рахунок формування подвійного електричного шару на межі розділу електрод/електроліт, а фарадеївські процеси відсутні. Питома ємність суперконденсаторів на основі отриманих за температури 800°С ПВМ становить 91-154 Ф/г, що зумовлено розвиненою мікропористою структурою матеріалів.

Ключові слова: пористий вуглецевий матеріал, імпедансна спектроскопія, суперконденсатор, питома поверхня, еквівалентна електрична схема.